Encapsulation of Peppermint Oil with Carboxymethyl *kappa* Carrageenan-Gelatine-Chitosan

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Encapsulation of Peppermint Oil with Carboxymethyl *kappa* Carrageenan-Gelatine-Chitosan

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Abstract. Peppermint oil is an essential oil that can provide fresh sensation but their fresh sensation will disappear in a short time. This research was designed to overcome that problem through encapsulating menthol oil in a term sensitive release microcapsule with carboxymethyl kappa carrageenan (CMKC) -gelatine-chitosan and crosslinking agent, lutensol, as microcapsule wall. Encapsulation of peppermint oil in a microcapsule is a chemical modification method for controlling the release of the component of peppermint oil to the environment. Microencapsulation of peppermint oil has been done by conservation method. Morphology of peppermint oil microcapsule was analyzed by Scanning Electron Microscope (SEM) image. The effect of temperature on the changes of microcapsule morphology was analyzed by optical microscope image. The effect of microcapsule heating temperature on the release of menthol oil component was analyzed by Gas Chromatography (GC) spectrum profile. Based on the observation of microcapsule morphology, without heating, the form of the microcapsule was round; after heated, the microcapsule became broken. There was a difference in the peppermint oil components releasing the power of microcapsule with different heating temperature; the quantity of each component of peppermint oil released when the microcapsule had been heating on 39 ºC was higher than on 36 ºC.

Keywords: Peppermint oil, CMKC, gelatine, chitosan, microcapsule

1. Introduction

In general, the characteristic of peppermint oil is very volatile. L- Menthol is the compound that is found in peppermint oil. L-Menthol is a cyclic terpene alcohol and the cause of peppermint oil widely used in pharmaceutical, cosmetic, and food [1]. Menthol can also stimulate a special receptor in the nervous system called TRPM8 to provide a cold sensation in the body [2]. Xing Body care industry now widely uses menthol as a giver of fresh and cold sensation. Unfortunately, their high volatile causes their application limited, their fresh and cold sensations quickly disappearing. To restrict the loss of L-Menthol during process or storage, it is useful to encapsulate it. Nowadays, microencapsulation is widely applied in protecting the volatile materials and its controllable release [1]

Microencapsulation is defined as the technology to packaging solids, a liquid or gaseous material with thin polymer coatings. The polymer acts as a protective film that can isolate the core. The protective membrane dissolves itself through a specific stimulus and then releases the core that has been arranged before. The application of this technology is widely utilized in some areas, such as

pharmaceutical, agricultural, medical, and food industries. Some factors that can lead to the rupture of microcapsules include temperature, pH, and solvent. Many kinds of microencapsulation methods are such as complex coacervation and freeze drying [3]. The complex method of conservation is an encapsulation process caused by separation phase. The formation of microcapsules by complex co-coacervation method is caused by the ability of anion coating material and cations that dissolve in water to interact form a phase that is rich in coatings called coacervate complex [1]. In the complex conservation process, two different charged polymers are under set conditions. In most cases, the proteinaceous biopolymers and a polysaccharide are used. Acidity, ionic strength, the amount of total solids, the rate of acidification, and the shear rate during acidification, are the factors that can affect complex formation and associative phase separations. The crosslinking agent is used to connect shell polymer [4]. CMKC is a modified polysaccharide biopolymer of k-carrageenan, which is a new innovation in the utilization of k-carrageenan; the derivatization of the -OH group ink-carrageenan into a carboxylic group increases the interaction of polymers with the polar environment [4] so that CMKC is more compatible interacting with polar formulations, compared with hydroxyl natural polysaccharides commonly used in making microcapsules. This study studied the use of CMKC as a component of forming peppermint oil microcapsule walls carried out by complex conservation methods.

2. Methods

2.1 Materials

Gelatine, chitosan, carboxymethyl kappa-carrageenan (CMKC), menthol extract, lutensol, demineralized water, and glacial acetic acid (CH_3COOH) p.a grade

2.2 Procedures

2.2.1 Microencapsulation of menthol oil using Gelatine/ CMKC/ Chitosan with complex coacervation methods using Lutensol as crosslinking agent

Each of Gelatine, Chitosan, CMKC, and Lutensol was weighed 0.1 g then dissolved in 20 mL water, then 2 mL menthol oil was added. The mixture was stirred at 700 rpm for 10 minutes. This solution was named as solution A. The A solution was wisely dropped into 1.45 % w/w of NaOH solution and stirred for 30 minutes at 700 rpm. The results were then separated by a separated funnel to be taken up.

2.2.2 Menthol oil component releasing profile analysis

The microcapsules were weighed 0.5 g then heated at 36 ^{0}C and 39 ^{0}C; the released compound was determined with Gas Chromatography (GC) Shimadzu 17A. The profile of component releasing the microcapsules was analyzed by GC chromatogram profile; the effect of temperature to the compound releasing profile of the microcapsule was analyzed by the number and the width of GC chromatogram peaks. The number of peaks showed the number of types of the compounds released, and the width of each peak area showed the intensity of the compound released.

2.2.3 Microcapsule morphology

Morphology of menthol microcapsule was analyzed by Scanning Electron Microscope (SEM) image, with FEI (SEM) EDAX, type: Inspect-S50. The effect of the enhancement of the microcapsule suspension environment temperature to microcapsule beads morphology was analyzed with an optical microscope; the suspension of microcapsule beads was spread onto two preparative glasses, and then the morphology of the microcapsule beads on the first preparative glass was observed, the second preparative glass that had spread with microcapsule suspension was heated on the hotplate surface (40 ^{o}C) and then observed.

3. Results and Discussion

Menthol is an essential oil that can provide a cool feeling sensation. Menthol is volatile, so its cold sensation quickly runs out. Microencapsulation is an effort to extend the time to feel their sensation by keeping the menthol oil inside a microcapsule shell. Microcapsules are one of the slow release preparation technologies that can be used to isolate the active ingredient and release it slowly. The microcapsules comprise the coating material (commonly from the polymer) and the active ingredient to be encapsulated. The coating material should be capable of forming a cohesive thin film with a core material, chemically mixed, not react to the core material.

In this research, chitosan, gelatine, CMKC, and lutensol were used as microcapsule shell material and menthol oil were used as core material ingredients. The shell material properties are one of the factors affecting the release of the core material. The system of the core material releasing control must be a factor when designing and choosing a microcapsule shell ingredient. The physicochemical properties and their interaction with the other ingredient and core material become the most important factor. The microcapsule shell ingredients used to capsulate menthol oil in this research were chosen for some reasons.

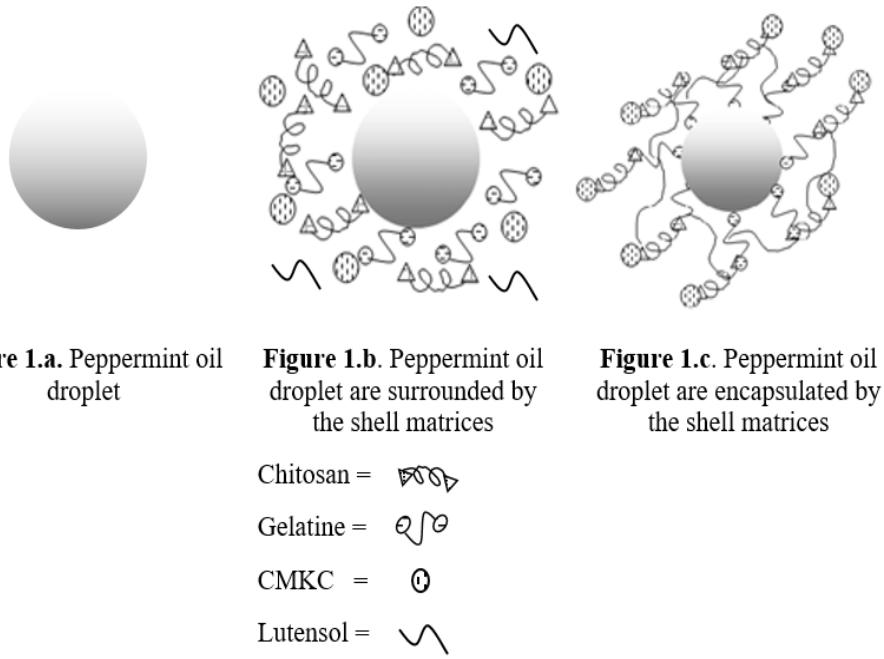

Figure 1.a. Peppermint oil droplet

Figure 1.b. Peppermint oil droplet are surrounded by the shell matrices

Figure 1.c. Peppermint oil droplet are encapsulated by the shell matrices

Figure 1. The illustration of peppermint oil microcapsule forming process

It is stated that physicochemical properties of CMKC are sensitive to the changes in their environment's acidity; when the acidity of the environment decreases, the interaction between CMKC molecules will decrease. The human body sweat contains some organic acid compounds; when the environmental temperature increases, the human body sweat increases, the degree of acidity of the skin will [5]**.**

The complex co-conservation method involves electrostatic attraction between two different polymers, charge. In the complex co-conservation method, when the cationic and anionic components are mixed, an interaction occurs, leading to the neutralization process forming a coacervate and will cover around the core as a microcapsule wall. A hydrophobic group of gelatine binds the menthol oil, a non-polar core material. The positive charge of chitosan functional groups is bound to the negative charge functional group of gelatine, and the negative charge of the CMKC group is bound to the positive charge group of citizens. In the complex co-

conservation, microcapsule structure is reinforced using a substance capable of forming crosslinks with gelatine. CMKC can act as a pH-responsive controller of peppermint oil released in the menthol microcapsule shell. In the production of microcapsules, gelatine is widely used because of its ability to bind to flavor compounds, biodegradablity, and low-cost. [5]They are used for the production of those materials in the food and pharmaceutical areas. Gelatine has a low melting point, <35 ^{O}C, the normal human body temperature is around 36 ^{o}C. As the one of microcapsule shell ingredient, gelatine causes the microcapsule broken when the microcapsule contacts with the human body. Chitosan acts as the backbone of the microcapsule shell; the backbone of composite commonly uses polymer, such as chitosan. In a cosmetic formulation, chitosan is very common because chitosan is very compatible. [6] The combination of chitosan and gelatine as the microcapsul shell has been done before by Nascimento [5]. In this research, we have explored the use of the combination of chitosan-gelatine-CMKC to make a thermal responsive microcapsule shell. Lutensol, a nonionic surfactant was added to crosslink the CMKC-gelatine-chitosan mix. Lutensol binds the strand of polymers that form the shell of microcapsule. The presence of crosslinking agents caused the structure of microcapsules sturdy so that the release of menthol was constant and gradually over long periods of time. The illustration of menthol oil microencapsulation process in this research is described in figure 1.

The microcapsules beads shape was round; after heated on a hot glass plate, some of the beads of the microcapsules became broken. The SEM image showed that the bubbles of the microcapsule beads appeared on the surface of the material; some of the bubbles had broken and left the hole. The release of menthol oil component was affected by heating temperature. The quantity menthol oil component released on higher heating temperature was higher than the lower heating temperature. The GC chromatogram of menthol oil component releasing intensity at 39 ^{o}C was higher than at 36 °C. The morphology of the microcapsules can be seen in Figure 2.

The broken of microcapsule granules caused peppermint oil to be released. The microcapsule shell consisting of CMKC-Gelatin-chitosan with lutensol binder easily broke with temperature stimulation. The GC chromatogram obtained from the measurement of the release of the components of peppermint oil from microcapsules heated at 36 ^{o}C and 39 ^{o}C showed the number and variety of peaks indicating that the type of compound released from microcapsules was identical. There was a difference in the height of each peak, in the GC chromatogram for measuring components released when the microcapsules were heated at different temperatures. Heating microcapsules at 39 ^{o}C produced a higher chromatogram than the heating of microcapsules at 39 ^{o}C. This phenomenon showed that the quantity of each component of peppermint oil was more released from microcapsules heated at 36 ^{o}C compared to those heated at 36 ^{o}C. In other words, temperature changes affected the core release of microcapsules. Figure 3 shows the chromatogram profile of GC release of peppermint oil component compounds heated at 36 ^{o}C and 39 ^{o}C.

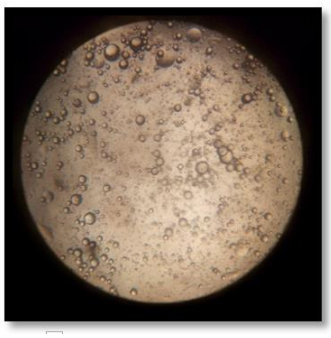

Figure 2.a. Optical microscopy image of the synthesized microcapsule

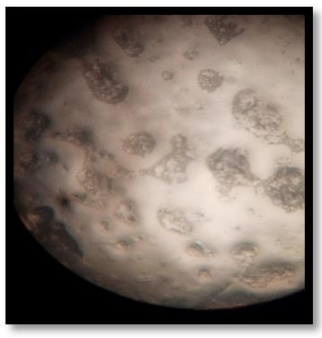

Figure 2.b. Optical microscopy image of the microcapsule synthesized after heated

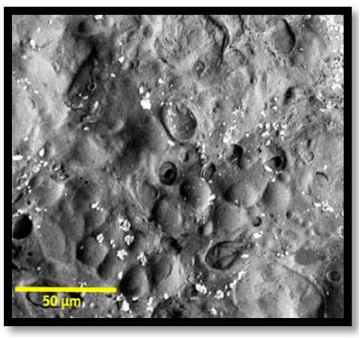

Figure 2.c. SEM image of the synthesized microcapsule

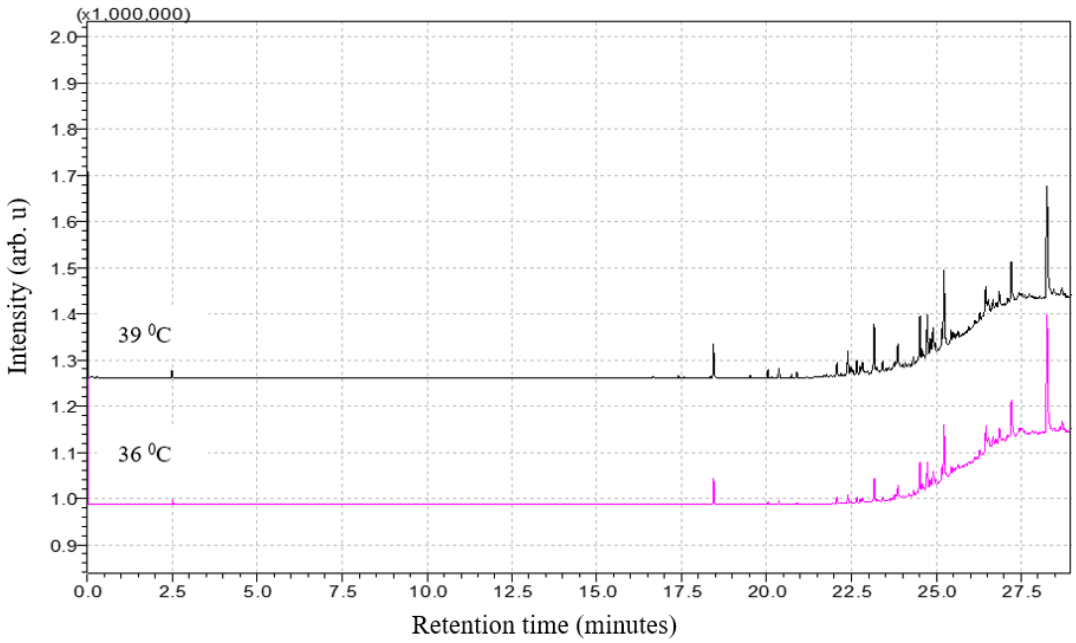

Figure 3. GC Chromatogram of peppermint oil compound released when the microcapsules suspension was heated at 36 °C and 39 °C

The microcapsule shell of peppermint oil microcapsule that will be a rupture and release of peppermint oil as a core controlled by the enhancement of temperature in human's body temperature range is the new innovation of volatile oil microencapsulation technology, this innovation is a very interesting idea to control the release of the aromatic oil matter commonly used in cosmetic.

4. Conclusion

The microencapsulation of peppermint oil with CMKC-gelatine-chitosan and lutensol as shell material, and peppermint oil as a core material, by complex coacervate methods, has been carried out. The microcapsules that were made had round shape and would be broken when heated. The release of peppermint oil compound from the microcapsule was affected by the environmental temperature; the higher the environmental temperature, the quantity of each component of peppermint oil that was released wolud be higher as well.

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